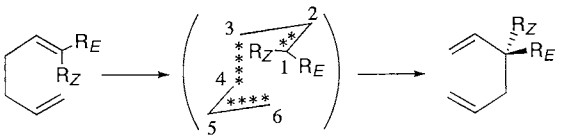
Geminal Bond Participation in the Cope Rearrangements of *Z*- and *E*-Substituted 1,5-Hexadienes and in the Reverse Reactions

Hirotaka Ikeda, Yuji Naruse, and Satoshi Inagaki*
Department of Chemistry, Faculty of Engineering, Gifu University, Yanagido, Gifu 501-1193

(Received January 11, 1999; CL-990027)

We analyzed the bond interactions at the transition state of the Cope rearrangement of 1,5-hexadiene to disclose the significant participation of the geminal σ bonds at the reacting centers. The electron-donating σ bonds at the *Z*-positions and the electron-accepting σ bonds at the *E*-positions in the 1-substituted 1,5-hexadienes were predicted from the geminal bond participation to enhance the reactivities. For the reverse reactions, the 3-substituted 1,5-hexadienes were similarly predicted to rearrange more readily into the 1-substituted ones with the electron-donating σ bonds at the *Z*-positions. The predictions were confirmed by the density functional theory calculations.

The Cope rearrangement is a well-known organic reaction (eq. 1).[1] There is *a priori* a question about the relative reactivities of *Z*- vs *E*-1-substituted 1,5-hexadienes. We analyzed the bond interactions at the transition state of the Cope rearrangement of 1,5-hexadiene to investigate the participation of the σ bonds geminal to the reacting π bonds, predicted the reactivities from the geminal bond participation, and confirmed the predictions by the density functional theory calculations.



(1)

1*E*, R_Z = H, R_E = CH_3
1*Z*, R_Z = CH_3, R_E = H
2*E*, R_Z = H, R_E = NH_2
2*Z*, R_Z = NH_2, R_E = H
3*E*, R_Z = H, R_E = OH
3*Z*, R_Z = OH, R_E = H
4*E*, R_Z = CH_3, R_E = SiH_3
4*Z*, R_Z = SiH_3, R_E = CH_3
5*E*, R_Z = NH_2, R_E = PH_2
5*Z*, R_Z = PH_2, R_E = NH_2
6*E*, R_Z = OH, R_E = SH
6*Z*, R_Z = SH, R_E = OH

We investigated the bond interactions at the transition state of the Cope rearrangement of 1,5-hexadiene by the method previously developed and successfully applied to a variety of molecular properties.[2] The interaction between the bond orbitals, *i* and *j*, was estimated by the interbond energy (IBE) and interbond population (IBP) defined as below:

$$IBE(i,j) = P_{ij}(H_{ij}+F_{ij}) \quad (2)$$
$$IBP(i,j) = 2P_{ij}S_{ij} \quad (3)$$

where P_{ij}, F_{ij}, H_{ij} and S_{ij} are the elements of the density, Fock, core Hamiltonian and overlap matrixes, respectively.

Table 1. Interbond energies (au) and interbond population at the transition state of the Cope rearrangement of 1,5-hexadiene

Interactions	IBE_{ij}	IBP_{ij}
$\sigma_{C_3-C_4} - \pi^*_{C_1-C_2}$	–0.9293	0.1320
$\pi_{C_1-C_2} - \sigma^*_{C_3-C_4}$	–0.6407	0.0968
$\pi_{C_1-C_2} - \pi^*_{C_5-C_6}$	–0.7261	0.0992
$\pi_{C_1-C_2} - \pi_{C_5-C_6}$	0.7100	–0.0943
$\sigma_{C_1-H_Z} - \pi^*_{C_5-C_6}$	–0.0177	0.0040
$\sigma_{C_1-H_E} - \pi^*_{C_5-C_6}$	0.0080	–0.0012
$\pi_{C_5-C_6} - \sigma^*_{C_1-H_Z}$	–0.0093	0.0010
$\pi_{C_5-C_6} - \sigma^*_{C_1-H_E}$	–0.0015	0.0002
$\sigma_{C_1-H_Z} - \sigma^*_{C_3-C_4}$	0.0034	–0.0007
$\sigma_{C_1-H_E} - \sigma^*_{C_3-C_4}$	0.0001	0.0000
$\sigma_{C_3-C_4} - \sigma^*_{C_1-H_Z}$	–0.0005	0.0001
$\sigma_{C_3-C_4} - \sigma^*_{C_1-H_E}$	–0.0286	0.0036

The calculated IBE and IBP values[3] are listed in Table 1. The interactions between the σ_{C3-C4} orbital and the π^*_{C1-C2} (π^*_{C5-C6}) orbital most stabilize the transition state (IBE = –0.9293, IBP = 0.1320). The stabilization due to the reverse delocalization from the π_{C1-C2} (π_{C5-C6}) orbitals to the σ^*_{C3-C4} orbital is relatively low (IBE = –0.6407, IBP = 0.0968). The stabilization for the interaction between the π_{C1-C2} orbital and the π^*_{C5-C6} orbital overcomes the repulsion between the π_{C1-C2} orbital and the π_{C5-C6} orbital (IBE = -0.7261, 0.7100).

A surprising difference was found in the σ electron delocalization from the σ_{C-H} bonds geminal to the π bond to the other π bond (Figure 1). The signs of the IBE and IBP values show that the delocalization is bonding (–0.0177, 0.0040) as usual from the σ_{C-HZ} orbital to the π^*_{C5-C6} orbital while that is antibonding from the σ_{C-HE} orbital (0.0080, –0.0012). The reverse delocalizations from the π_{C5-C6} bond to the σ_{C-HZ} and σ_{C-HE} bonds occur to a less extent (IBE = –0.0093, –0.0015, respectively).

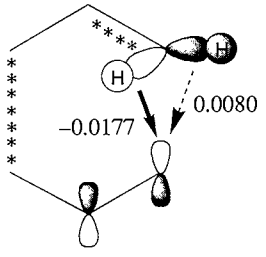


Figure 1. Geminal bond participation.

Copyright © 1999 The Chemical Society of Japan

Another significant difference was found in the σ electron delocalization from the σ_{C3-C4} bond to the σ_{C-HZ} and σ_{C-HE} bonds. The stabilizing delocalization to the σ^*_{C-HE} orbital (IBE = –0.0286, 0.0036) is greater than that to the σ^*_{C-HZ} orbital (IBE = –0.0005, 0.0001). The delocalizations in the opposite direction contribute to a little extent.

The participation of the geminal σ bonds at the reacting centers leads to a prediction that a relatively electropositive atom or substituent at the *Z*-position and electronegative one at the *E*-position enhance the reactivity of the hexadienes. An electropositive atom raises the σ bonding orbital energy to increase the bonding delocalization from the geminal σ bond at the *Z*-position to the π_{C5-C6} bond. An electronegative atom lowers the σ bonding orbital energy to decrease the antibonding delocalization from the σ bond at the *E*-position and to increase the stabilizing delocalization from the σ_{C3-C4} bond to the σ bond at the *E*-position.

Table 2. Activation energies[a] (kca/mol) of the Cope rearrangements of *Z*- and *E*-1-substituted 1,5-hexadienes and energy differences[a] (kca/mol) between the *Z*- and *E*-isomers in the reactants and the transition states

Dienes	$\Delta E_E^{\ddagger}$[b]	$\Delta E_Z^{\ddagger}$[b]	$\delta\Delta E^{\ddagger}$[c]	ΔE_R[d]	ΔE_{TS}[d]
1	36.3	36.7	0.4	1.60	2.04
2	37.5	38.6	1.0	0.72	1.75
3	37.2	38.7	1.5	0.09	1.56
4	39.0	38.0	–1.0	0.45	–0.51
5	41.6	38.1	–3.6	1.17	–2.46
6	38.1	36.5	–1.6	1.29	–0.27

[a]B3LYP/6–31G* energies including zero-point energies. [b]Activation energies based on the most stable rotatomer. [c]$\delta\Delta E^{\ddagger} = \Delta E_Z^{\ddagger} - \Delta E_E^{\ddagger}$. [d]Energy differences in the reactants, ΔE_R, and those in the transition states, ΔE_{TS}. $\Delta E = E$ (*Z*-isomer) – E (*E*-isomer).

We calculated the relative reactivities of *Z*- vs *E*-1-substituted 1,5-hexadienes in order to confirm the prediction.[5] The *E*-isomers of the dienes **1–3** substituted by the methyl, amino, and hydroxy groups have a relatively electropositive C–H bond at the *Z*-position and then were predicted to be more reactive than the *Z*-isomers. This was in agreement with the calculated activation energies of the reactions (Table 2). Moreover, we compared the relative reactivities of the *Z*- vs *E*-isomers **4–6** with the substituent atoms in the same group of the periodic table. The second-row element substituents at the *Z*-position were predicted to enhance the reactivity rather than those at the *E*-position. The predictions were confirmed by the calculated relatively low activation energies of the *Z*-isomers. The high reactivities of *Z*-isomers ruled out the steric control and supported the geminal bond participation in the Cope rearrangements.

The calculations of most of the reactions examined supported the hypothesis that the reactivities should be controlled by the stabilization of the transition state.

The 1-substituted 1,5-hexadienes would be more favored at the equilibrium in the Cope rearrangements than the 3-substituted ones. The 3-substituted 1,5-hexadienes are suitable reactants to examine the reactivities experimentally. The reactant molecules leading to the *Z*- and *E*-transition states are identical with each other in the reactions of the 3-substituted 1,5-hexadienes. The activation energy difference is determined by the transition energy difference. The geminal bond participation is directly applied. The main products are predicted to be the 1-substituted 1,5-hexadienes with the relatively electropositive substituents at the *Z*-1-position.

In summary, the relative reactivities of 1,5-hexadienes in the Cope rearrangements are controlled by the geminal bond participation. Electron-donating σ bonds at the *Z*-positions and electron-accepting σ bonds at the *E*-positions facilitate the reactions of 1-substituted 1,5-hexadienes and their formation in the reverse rearrangements.

References and Notes

1 For example, see: a) S. H. Pine, J. B. Hendrickson, D. J. Cram, and G. S. Hammond, "Organic Chemistry," McGraw-Hill, New York (1980). b) J. March, "Advanced Organic Chemistry," John Wiley & Sons, Canada (1992).

2 a) S. Inagaki, N. Goto, and K. Yoshikawa, *J. Am. Chem. Soc.*, **113**, 7144 (1991). b) S. Inagaki, K. Yoshikawa, and Y. Hayano, *J. Am. Chem. Soc.*, **115**, 3706 (1993). c) S. Inagaki, Y. Ishitani, and T. Kakefu, *J. Am. Chem. Soc.*, **116**, 5954 (1994). d) S. Inagaki, T. Kakefu, T. Yamamoto, and H. Wasada, *J. Phys. Chem.*, **100**, 9615 (1996). e) S. Inagaki, T. Yamamoto, and S. Ohashi, *Chem. Lett.*, **1997**, 977.

3 Our original program was employed to analyze the bond interactions at the chair-form transition state optimized by the *ab initio* molecular orbital calculation[4] at the RHF level. The 6–31G* basis set was used.

4 Gaussian 94, Revision C.3, M. J. Frisch, G. W. Trucks, H. B. Schlegel, P. M. W. Gill, B. G. Johnson, M. A. Robb, J. R. Cheeseman, T. Keith, G. A. Petersson, J. A. Montgomery, K. Raghavachari, M. A. Al-Laham, V. G. Zakrzewski, J. A. Ortiz, J. B. Foresman, J. Cioslowski, B. B. Stefanov, A. Nanayakkara, M. Challacombe, C. Y. Peng, P. Y. Ayala, W. Chen, M. W. Wong, J. L. Andres, E. S. Reploge, R. Gomperts, R. L. Martin, D. J. Fox, J. S. Binkley, D. J. Defrees, J. Baker, J. P. Stewart, M. Head-Gordon, C. Gonzalez, and J. A. Pople, Gaussian, Inc., Pittsburgh, PA (1995).

5 The geometry optimization was carried out by the density functional theory calculations at the B3LYP/6-31G* level,[4] which were reported to give the values matching the experimental results closely.[6] All geometries examined here were checked by the frequency calculations.

6 O. Wiest, D. C. Montiel, and K. N. Houk, *J. Phys. Chem. A*, **101**, 8378 (1997).